PB-229 943

TRACE METAL STUDY - ALLEGHENY, MONONGAHELA AND OHIO RIVERS, PITTSBURGH, PENNSYLVANIA AREA

Federal Water Pollution Control Administration
Wheeling, West Virginia

February 1968

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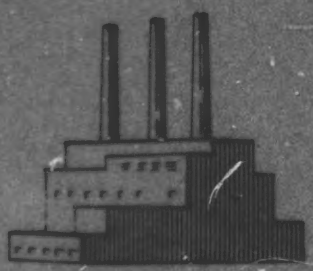

UNITED STATES DEPARTMENT OF THE INTERIOR
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TRACE METAL STUDY

ALLEGHENY, MONONGAHELA AND OHIO RIVERS

PITTSBURGH, PENNSYLVANIA AREA

Work Document No. 14

This document has been prepared to record a specific water pollution control activity carried out to date in the furtherance of the water pollution control program being developed in the Ohio River Basin. The information contained herein will serve as a ready reference to aid in the planning and development of the program in the Basin, for appropriate in-service training of participating personnel, and facilitating program activities with other cooperating groups.

Questions or comments relative to this material should be directed to:

Laboratory Services Section
Wheeling Field Station
Ohio River Basin Project
Wheeling, West Virginia

UNITED STATES DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
OHIO BASIN REGION

February 1968

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I. INTRODUCTION

During water year 1965, a study of the water quality at critical points on the Monongahela, Allegheny and Ohio Rivers in the Pittsburgh, Pennsylvania, area was performed by the University of Pittsburgh under contract with the Federal Water Pollution Control Administration. Data from this study has been analyzed to determine effects of various trace metals on the water quality of the upper Ohio River basin in the Pittsburgh area.

The data used was from seven sampling stations on the Ohio and its primary tributaries in western Pennsylvania. The four sampling stations upstream of Pittsburgh were located on the Allegheny, Kiskiminetas, Monongahela and Youghiogheny Rivers. Three stations were located in or below Pittsburgh, Pennsylvania.

II. SUMMARY OF FINDINGS

1. The U. S. Public Health Service has established trace metal limits for public water supplies for 10 out of the 18 elements tested.
2. No information of trace metal concentrations in finished drinking water, using these river supply sources, is known at this time.
3. The highest concentrations of most trace metals have occurred in the Kiskiminetas and the upper Monongahela Rivers. Heavy mining operations in these areas have contributed most of these trace metal concentrations.
4. Arsenic test data exceeded the limits set by the U. S. Public Health Service; however, the test is known to produce high values because of iron interference.
5. Cadmium exceeded the USPHS limits, but the minimum detection level of the test and the PHS limit are at the same level.
6. The average concentrations of iron and manganese were higher than desired for all stations, but USPHS limits for these elements are not based on physiological considerations.

III. STUDY DESCRIPTION

Sample Stations

Seven sampling stations were chosen by the University of Pittsburgh and FWPCA to give the best representation of water quality above and below the Pittsburgh metropolitan area.

The first of these stations was located on the upper Allegheny River at Parker, Pennsylvania. Because of changes occurring at this station, a replacement was chosen at Kittanning. A second site was chosen on the Kiskiminetas River which is the major tributary to the Allegheny in the Pittsburgh area. The third site selected was on the upper Monongahela River at Belle Vernon, Pennsylvania, and a fourth on its major tributary, the Youghiogheny River. These four stations are upstream of the Pittsburgh metropolitan area.

Two other stations were chosen near the Point or Golden Triangle of Pittsburgh in the downtown area. One station was selected on the lower Allegheny and one on the lower Monongahela above the confluence of these rivers which form the Ohio River. The final station was located about 25 miles downstream on the Ohio to measure the pollutional load of the lower Pittsburgh area.

The stations' descriptions are as follows:

Station Number	River Miles from Pittsburgh	Location
550	25.20	Ohio River at Rochester, Pennsylvania
551	0.76	Monongahela River at Smithfield Bridge
552	35.50	Youghiogheny River at West Newton, Pennsylvania
553	43.32	Monongahela River at Belle Vernon, Pennsylvania

Station Number	River Miles from Pittsburgh	Location
851	0.58	Allegheny River at Sixth Street Bridge, Pittsburgh, Pennsylvania
852	43.50	Kiskiminetas River at Apallo, Pennsylvania
853	83.50	Allegheny River at Parker, Pennsylvania
854	45.11	Allegheny River at Kittanning, Pennsylvania

Sampling

The sampling program covered one water year beginning in October 1964 and ending in September 1965. Samples were collected weekly or biweekly by the University of Pittsburgh and reserved for monthly compositing in proportion to the recorded flows at each station. All trace metal samples were analyzed using spectrographic techniques by the Federal Water Pollution Control Administration's Laboratory, Division of Pollution Surveillance, Cincinnati, Ohio.

All sampling was performed from highway bridges to save time and expense involved with boat sampling. Wherever possible collection was from the downstream side of the bridge, which allowed better access and freedom of sampling especially when stream flow was high.

IV. TRACE METAL ANALYSES

A discussion is presented below for the concentrations of various trace metals found in the Pittsburgh area. The tabulation of data appear in Appendix A, graphs for the trace metals which have established limits appear in Appendix B and a complete discussion of each metal characteristic is presented in Appendix C.

Many of the individual analysis were at the minimum detectable limit for emission spectroscopy, such as cadmium, so that results were preceded by less than signs. These signs were used in Appendix A where applicable in the columns marked "Range of Concentration" and "Average". The graphs in Appendix B were plotted without regard to the less than sign, so that they should be used only in conjunction with the tables in Appendix A. The metal characteristic section in Appendix C should be reviewed for metals of interest.

It is known that some interferences cause certain elements to indicate higher than absolute values such as arsenic. The results in this report are based on the best judgment that could be provided for the data available. This analytical work was done entirely by the spectroscopists at the Cincinnati Laboratory.

Aluminum values in the study area ranged from 22 to 3375 ug/l. The highest values were from the Kiskiminetas River and the Upper Monongahela River. The aluminum originates mostly from coal mining activity. No aluminum limits have been established for water supplies.

Average arsenic concentrations for each of the seven stations ranged from <42 to 232 ug/l with an overall average of 116 ug/l. It is known that high iron concentrations interfere with the arsenic spectrum causing results to be

questionable at these low levels. Some arsenic could be contributed by coal mine drainage in the Kiskiminetas and Monongahela Rivers. It is suggested that future work be followed up by wet chemical analyses when arsenic concentrations exceed 50 ug/l.

Barium does not constitute a problem in the Pittsburgh area. The highest concentration found was 67 ug/l, which is well below the 1000 ug/l rejection limit for water supplies. Barium concentrations ranged from 15 to 52 ug/l for all stations. The greatest concentrations were found in the Allegheny River in the Parker-Kittanning, Pennsylvania, area.

The average beryllium concentrations ranged from <0.06 to 0.64 ug/l among stations. A high value of 1.75 ug/l was found for beryllium at Apollo, Pennsylvania, on the Kiskiminetas River. No limit has been set for comparison. Some of these values were among the highest ever found by the Cincinnati FWPCA laboratory for any water samples.

Individual boron values ranged from 39 to 330 ug/l with the highest station average (206 ug/l) occurring at Apollo, Pennsylvania, on the Kiskiminetas River. No limits have ever been set for boron.

The average cadmium concentration for all stations ranged from <12 to 27 ug/l with an overall average near 19 ug/l. It should be noted that the minimum detection limit of 10 ug/l is the same as the mandatory limit for the 1962 Drinking Water Standards. This makes any examination of data with respect to higher than desired concentrations difficult to discuss. For all practical purposes, cadmium is not considered to be a problem in this area at this time.

Total chromium was present in most samples in slight amounts (<3-22 ug/l). The rejection limit for hexavalent chromium in a water supply is 50 ug/l. No

samples exceeded this value for total chromium, therefore, it is apparent that hexavalent chromium was not exceeded. The highest single total chromium value was 22 ug/l found in the Monongahela River at Belle Vernon, Pennsylvania.

The overall range of cobalt stations was <5 to 60 ug/l. The highest concentrations of cobalt occurred in the Monongahela River at Belle Vernon and the Kiskiminetas River at Apollo, Pennsylvania, with averages of 16 and 23 ug/l, respectively. No limit has been prescribed for cobalt.

The acceptable maximum limit for copper in water supplies is 1000 ug/l. No copper concentration exceeded 300 ug/l in the Pittsburgh area. The highest average for any station was 91 ug/l and the highest value throughout the study area was 300 ug/l at Belle Vernon on the Monongahela River.

Iron was found in the highest average concentrations on the Kiskiminetas River (1585 ug/l) and Upper Monongahela River (1882 ug/l). The overall range was 100 to 5000 ug/l. The recommended limit of 300 ug/l for iron was exceeded 89% of the time. The higher concentrations are a result of extensive mining in the upstream areas of these two rivers. Iron is more a taste problem than a physiological condition.

The average lead concentration was less than 50 ug/l for all stations with the highest lead average (36 ug/l) occurring at Belle Vernon, Pennsylvania, on the Monongahela River. Only two lead values out of 72 samples tested for the basin exceeded the recommended limits. Lead concentrations of 88 and 92 ug/l were found at Belle Vernon, Pennsylvania, on the Monongahela River. Lead concentrations at these levels have occurred occasionally throughout the county in water supplies. Lead is not considered to be a problem in this area at this time.

The greatest manganese concentrations occurred in the Kiskiminetas and lower Allegheny Rivers. The recommended limit of 50 ug/l was exceeded 97 1/2% of the time throughout the study area. Values from all stations ranged from 28 to 1500 ug/l with an average of 61 ug/l on the upper Allegheny and 772 ug/l in the Kiskiminetas River at Apollo, Pennsylvania. The manganese limit is based on esthetic and economic considerations rather than physiological hazards.

Most samples contained molybdenum at low levels. Values ranged from <8 to 400 ug/l with the highest value occurring in the Kiskiminetas River. No molybdenum limits have been recommended.

Nickel, which is found in coal mine drainage, was most apparent in the Kiskiminetas River at Apollo, Pennsulvania, the Monongahela River at Belle Vernon, Pennsylvania, and its mouth, and in the Ohio River at Rochester, Pennsylvania. The highest average value for all stations was 57 ug/l. The highest single value of 138 ug/l was found at Apollo, Pennsylvania, on the Kiskiminetas River. No limits have been recommended for nickel.

Silver was found in low concentrations at most stations. The highest value of 5 ug/l at Rochester, Pennsylvania, in the Ohio River should cause no concern when compared to a limit of 50 ug/l.

Overall values for strontium ranged from 15 to 175 ug/l with the highest average (94 ug/l) occurring at the mouth of the Monongahela River. No limits have been recommended for strontium.

Vanadium was found at all stations with an overall range of <10-88 ug/l. The highest concentration (88 ug/l) occurred at Belle Vernon, Pennsylvania, in the Monongahela River. No limits have been established for vanadium in public water supplies.

Zinc was found at all sampling stations with an overall range of 10 to 504 ug/l. The averages between stations ranged from 16 to 208 ug/l. However, all values were considerably less than the recommended limit of 5000 ug/l.

It appears from the above examination of trace metal data that coal mine drainage contributes a much greater concentration of trace metals than from sources of industrial pollution. This study was not intended to isolate and pinpoint individual sources of trace metal polluters.

APPENDIX A

Pittsburgh Area
Trace Metals Data Tabulation

ALUMINUM (ug/l)

Station Number	USPHS Recommended Limit	Number of Samples	Range of Concentration	Number Exceeding Limit	Average
853 (Allegheny River @ Parker, Pa.)	None	3	75-500	---	220
854 (Allegheny River @ Kittanning, Pa.)	None	9	25-800	---	376
852 (Kiskiminetas River @ Apollo, Pa.)	None	12	670-3375	---	1587
851 (Allegheny River @ Pittsburgh, Pa.)	None	12	29-1438	---	501
553 (Monongahela River @ Belle Vernon, Pa.)	None	12	233-2700	---	1199
552 (Youghiogheny River @ West Newton, Pa.)	None	12	40-750	---	294
551 (Monongahela River @ Pittsburgh, Pa.)	None	12	25-1500	---	462
550 (Ohio River @ Rochester, Pa.)	None	12	22-1875	---	472

ARSENIC
(ug/l)

Station Number	USPHS Recommended Limit	Number of Samples	Range of Concentration	Number Exceeding Limit	Average
853	50	3	<25-50	0	<42
854	50	9	<50-70	2	<53
852	50	12	<50-600	11	<232
851	50	12	<25-230	5	<80
553	50	11	<25-308	6	<126
552	50	12	<50-350	9	<143
551	50	11	<25-250	6	<84
550	50	12	<25-275	8	<98

BARIUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	1000	3	40-67	0	52
854	1000	9	3-53	0	32
852	1000	12	5-30	0	15
851	1000	12	8-59	0	34
553	1000	12	6-36	0	20
552	1000	12	9-53	0	24
551	1000	11	10-34	0	20
550	1000	12	8-38	0	24

BERYLLIUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	None	3	<0.05-0.08	---	<0.06
854	None	9	<0.03-0.13	---	<0.07
852	None	12	0.30-1.75	---	0.64
851	None	12	<0.05-0.21	---	<0.11
553	None	12	0.12-1.13	---	0.3
552	None	12	<0.03-0.17	---	<0.09
551	None	11	<0.05-0.13	---	<0.08
550	None	12	<0.05-0.13	---	<0.07

BORON
(ug/l)

Station Number	USPHS Recommended Limit	Number of Samples	Range of Concentration	Number Exceeding Limit	Average
853	None	3	62-76	---	71
854	None	9	39-73	---	52
852	None	12	93-330	---	206
851	None	12	60-155	---	100
553	None	12	51-154	---	98
552	None	12	45-150	---	99
551	None	11	74-210	---	126
550	None	12	60-320	---	154

CADMIUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	10	3	<10-17	1	<12
854	10	9	<10-25	6	<15
852	10	12	<10-25	11	<19
851	10	12	<17-33	12	<21
553	10	11	<10-88	9	<27
552	10	12	<10-33	9	<18
551	10	11	<10-25	10	<18
550	10	12	<17-25	12	<19

CHROMIUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	50	3	<4-18	0	<12
854	50	9	<3-16	0	<7
852	50	12	<3-6	0	<4
851	50	12	<4-17	0	<7
553	50	11	<3-22	0	<8
552	50	12	<3-9	0	<5
551	50	11	<4-8	0	<5
550	50	12	<4-12	0	<8

COBALT
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	None	3	<5-8	---	<6
854	None	9	<5-13	---	<8
852	None	12	<7-60	---	<23
851	None	12	<8-20	---	<11
553	None	11	<5-44	---	<16
552	None	12	<5-17	---	<9
551	None	11	<5-13	---	<9
550	None	12	<8-13	---	<9

COPPER
(ug/l)

Station Number	USPHS Recommended Limit	Number of Samples	Range of Concentration	Number Exceeding Limit	Average
853	1000	3	4-12	0	7
854	1000	9	4-38	0	17
852	1000	12	4-100	0	20
851	1000	12	14-97	0	30
553	1000	12	8-300	0	91
552	1000	12	1-168	0	10
551	1000	11	6-50	0	25
550	1000	12	5-37	0	22

IRON
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	300	3	160-500	1	276
854	300	9	100-1200	6	529
852	300	12	670-4000	12	1585
851	300	12	248-2490	10	884
553	300	11	225-5000	9	1882
552	300	12	500-2490	12	1228
551	300	11	378-5000	12	1457
550	300	12	390-5000	12	1346

LEAD
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	50	3	<10-17	0	<12
854	50	9	<10-50	0	<20
852	50	12	<13-30	0	<19
851	50	12	<17-40	0	<23
553	50	11	<10-92	2	<36
552	50	12	<10-33	0	<19
551	50	11	<10-25	0	<18
550	50	12	<17-26	0	<20

MANGANESE
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	50	3	36-77	2	61
854	50	9	28-550	8	256
852	50	12	335-1500	12	772
851	50	12	420-1000	12	664
553	50	11	299-900	12	474
552	50	12	175-291	12	240
551	50	11	250-800	12	450
550	50	12	400-1000	12	569

MOLYBDENUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range of Concentration	Number Exceeding Limit	Average
853	None	3	<8-30	---	<18
854	None	9	<10-110	---	<40
852	None	12	<8-400	---	<108
851	None	12	<8-200	---	<46
553	None	12	<8-200	---	<52
552	None	12	<10-113	---	<35
551	None	12	<8-150	---	<44
550	None	12	<8-150	---	<64

NICKEL
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range Of Concentration	Number Exceeding Limit	Average
853	None	3	<5-8	---	<6
854	None	9	<5-13	---	<8
852	None	12	11-138	---	57
851	None	12	<8-44	---	<23
553	None	12	<8-60	---	<25
552	None	12	<5-17	---	<10
551	None	11	<8-20	---	<40
550	None	12	<8-70	---	<21

SILVER
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range Of Concentration	Number Exceeding Limit	Average
853	50	3	<0.5-0.8	0	<0.6
854	50	9	<0.5-1.3	0	<0.8
852	50	12	<0.5-1.3	0	<0.9
851	50	12	<0.8-4.0	0	<1.3
553	50	12	<0.5-4.0	0	<1.3
552	50	12	<0.5-1.7	0	<0.9
551	50	11	<0.5-1.3	0	<0.9
550	50	12	<0.8-5.0	0	<1.3

STRONTIUM
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range Of Concentration	Number Exceeding Limit	Average
853	None	3	22-100	---	62
854	None	9	15-82	---	38
852	None	12	26-80	---	51
851	None	12	28-130	---	74
553	None	11	26-156	---	76
552	None	12	15-73	---	38
551	None	11	35-175	---	94
550	None	12	31-140	---	86

VANADIUM
(ug/l)

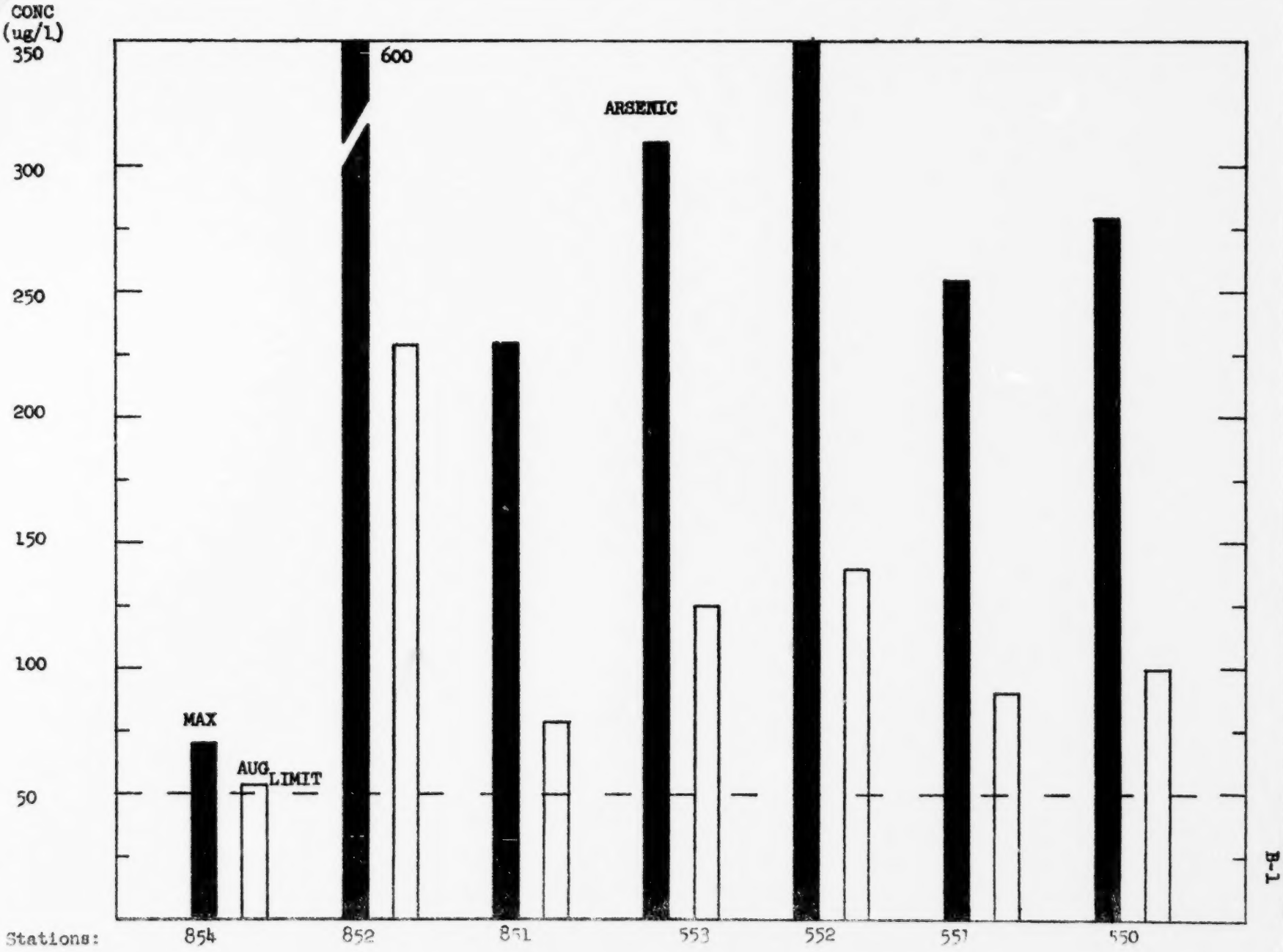
Station Number	USPHS Recommended Limit	Number Of Samples	Range Of Concentration	Number Exceeding Limit	Average
853	None	3	<10-17	---	<12
854	None	9	<10-25	---	<16
852	None	12	<10-25	---	<17
851	None	12	<17-33	---	<21
553	None	12	<10-88	---	<26
552	None	12	<10-33	---	<19
551	None	11	<10-25	---	<18
550	None	12	<17-20	---	<19

ZINC
(ug/l)

Station Number	USPHS Recommended Limit	Number Of Samples	Range Of Concentration	Number Exceeding Limit	Average
853	5000	3	11-24	0	16
854	5000	9	10-47	0	28
852	5000	12	70-465	0	245
851	5000	12	38-180	0	88
553	5000	12	50-504	0	208
552	5000	12	20-70	0	38
551	5000	11	26-180	0	97
550	5000	12	34-126	0	75

APPENDIX B

Graphs of Concentrations and Limits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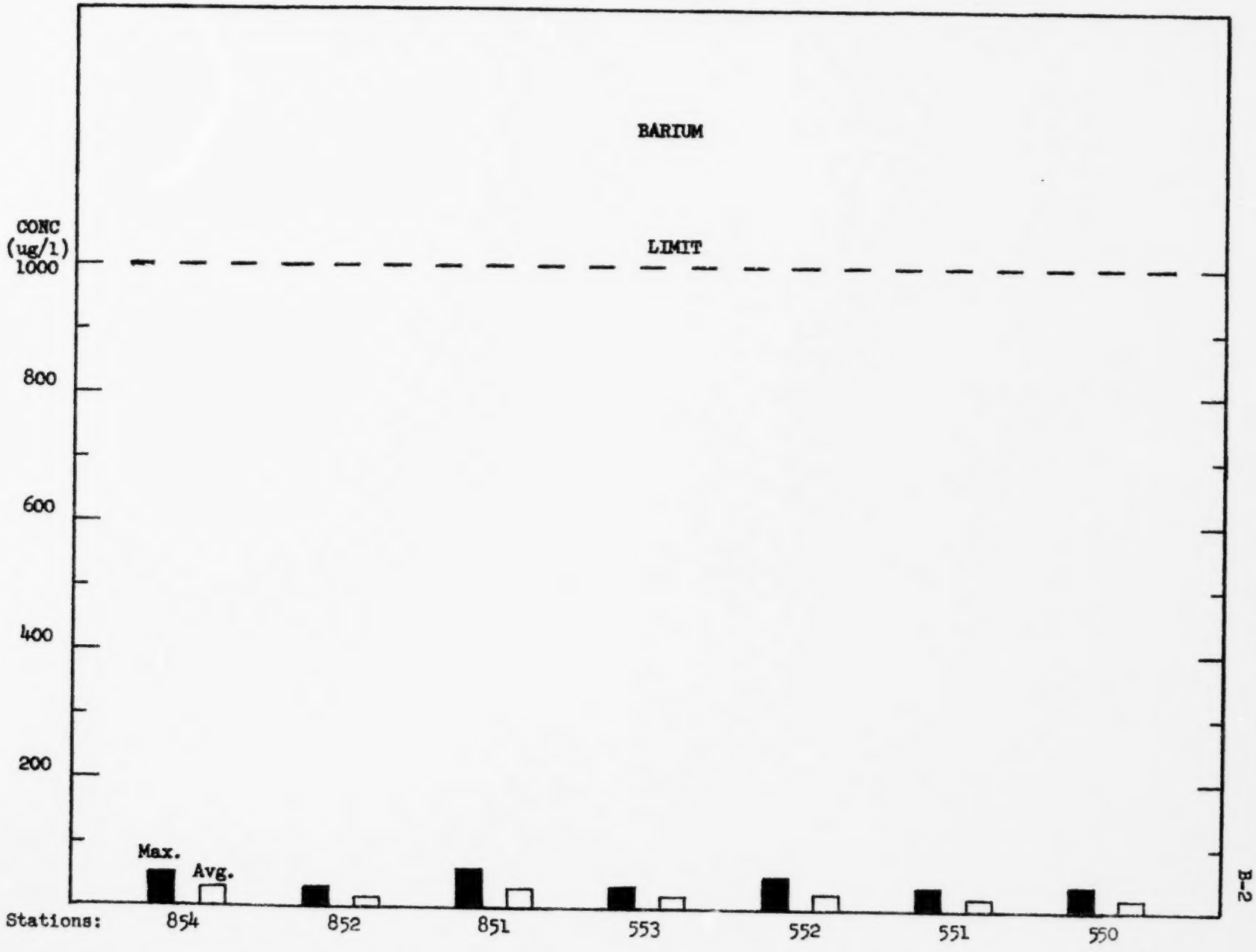
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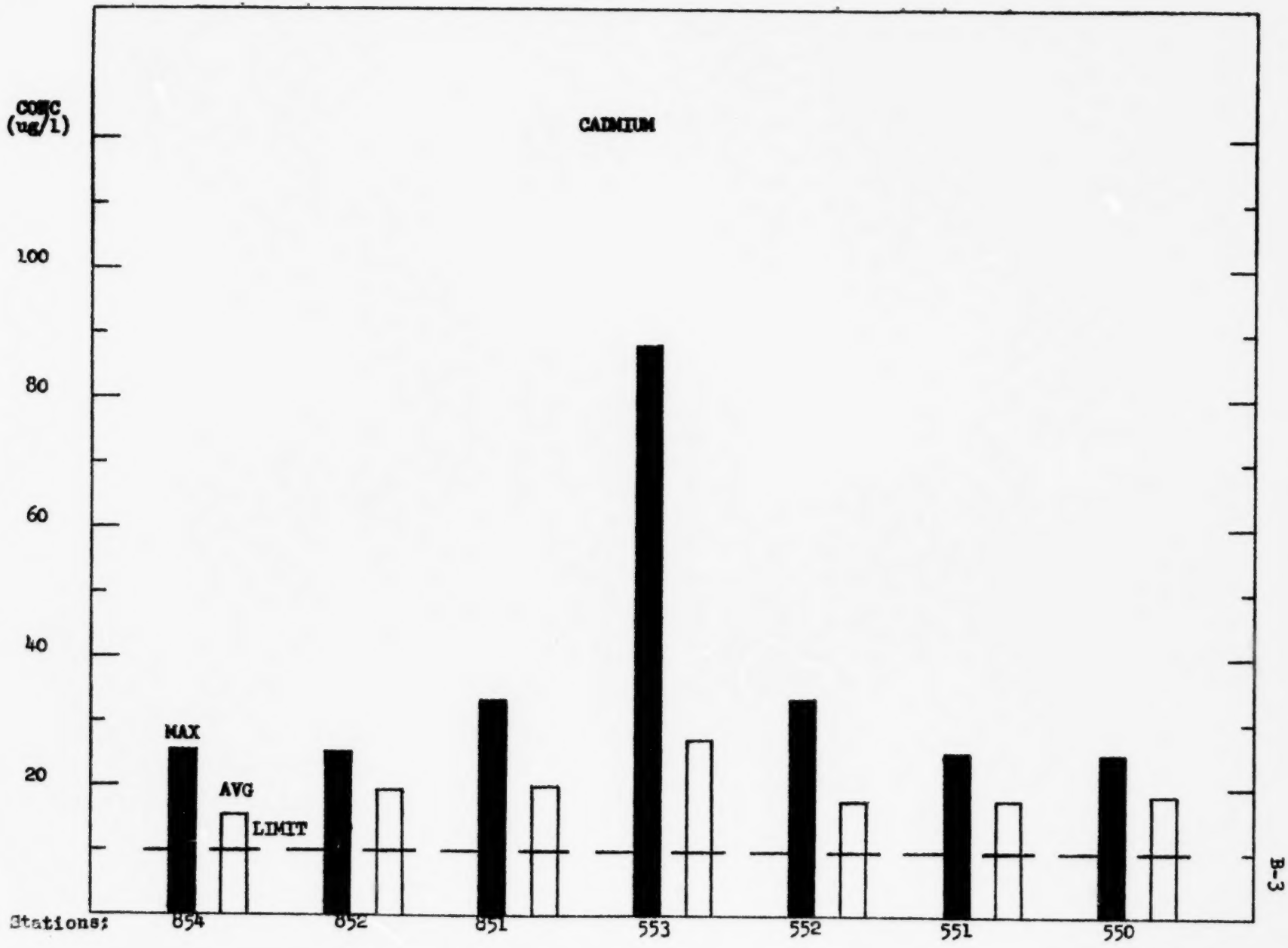
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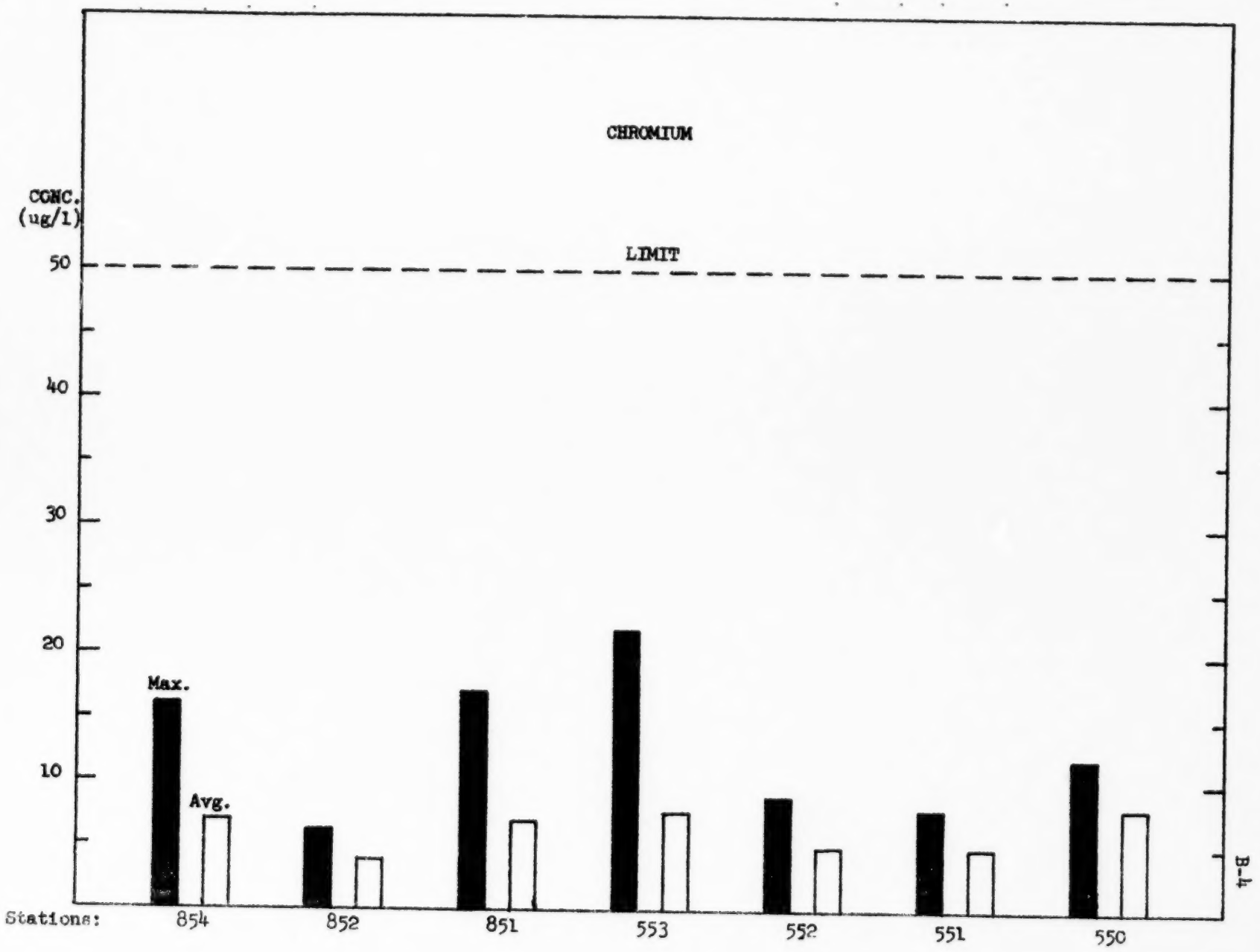
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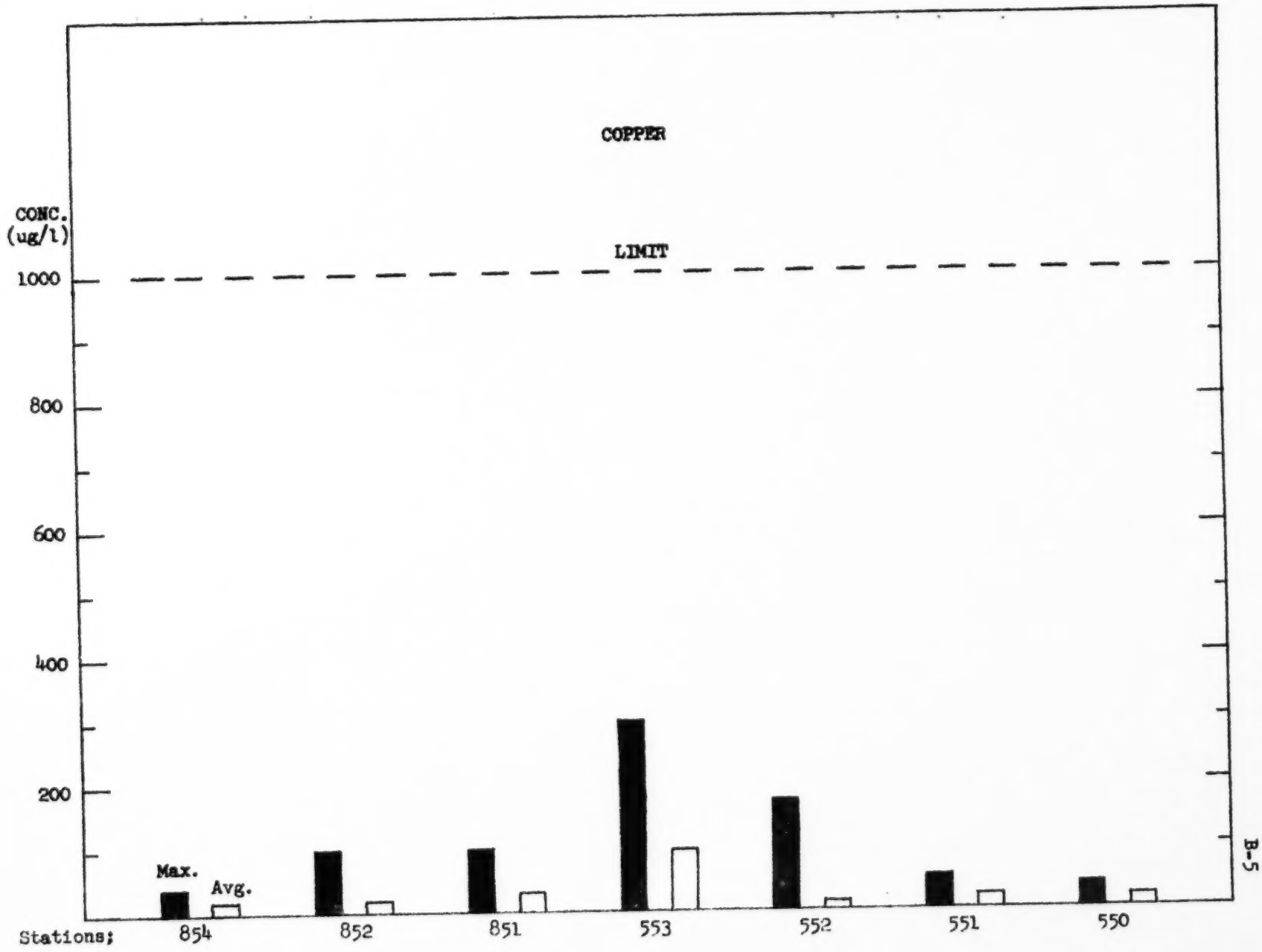
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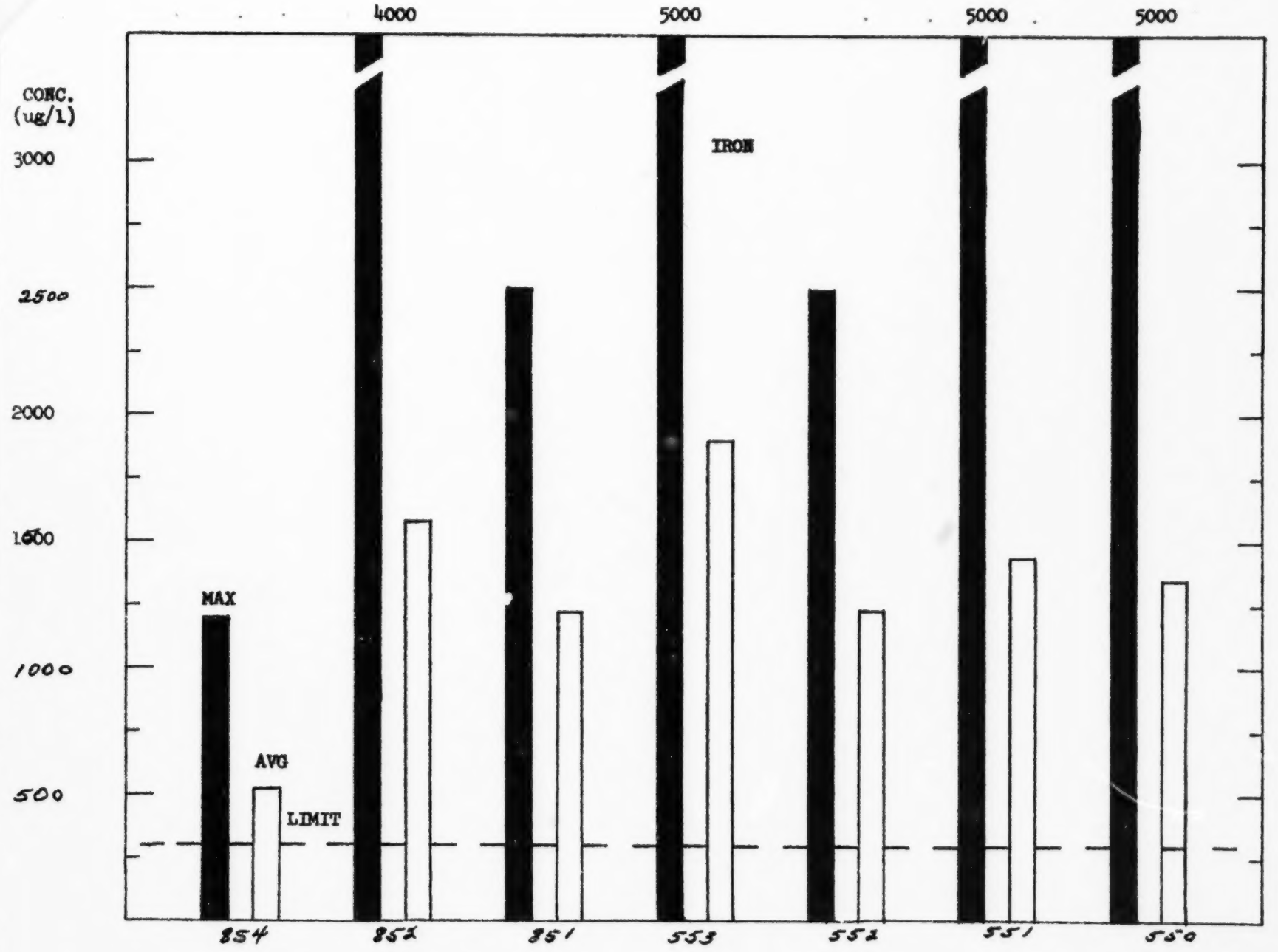
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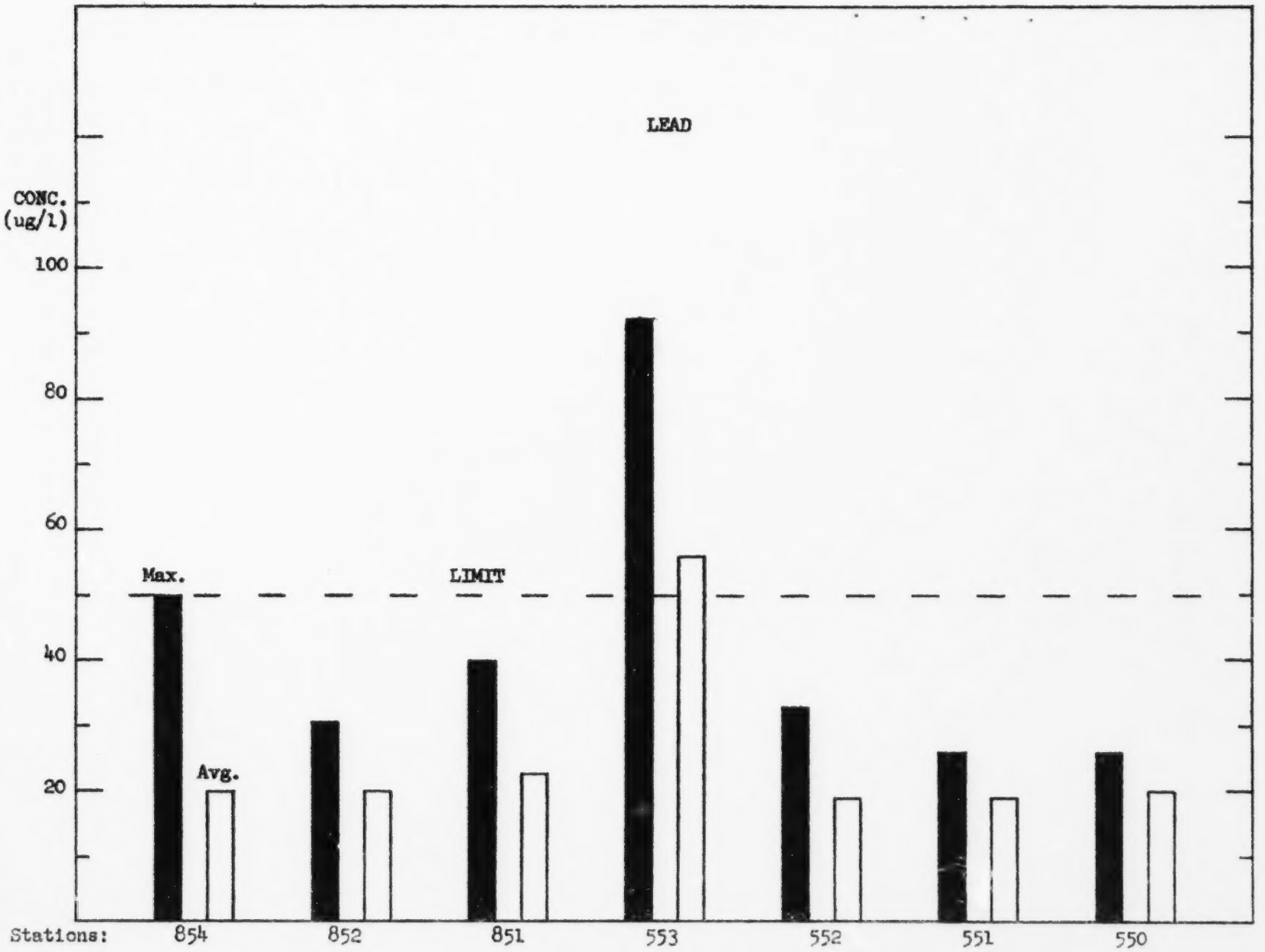
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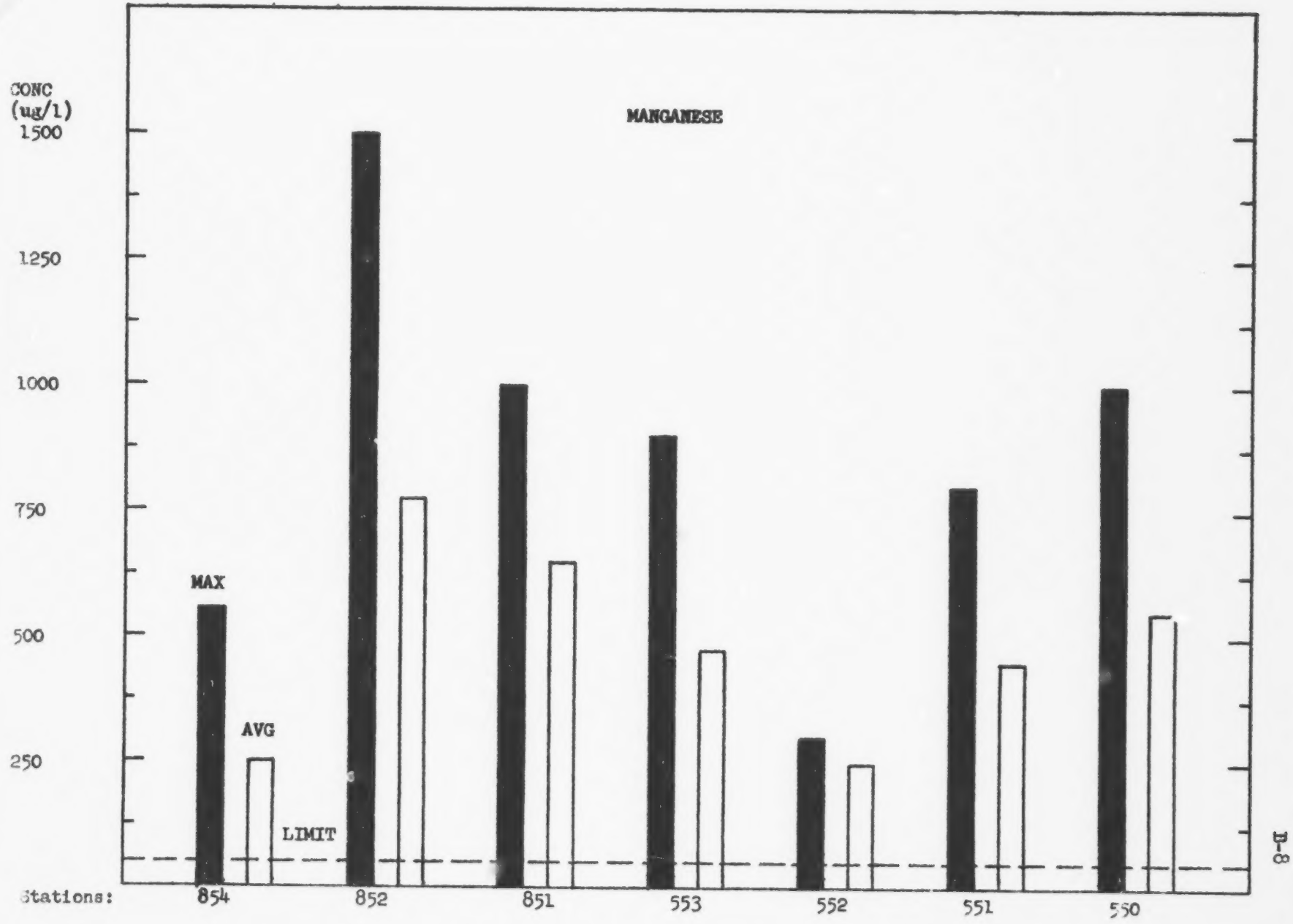
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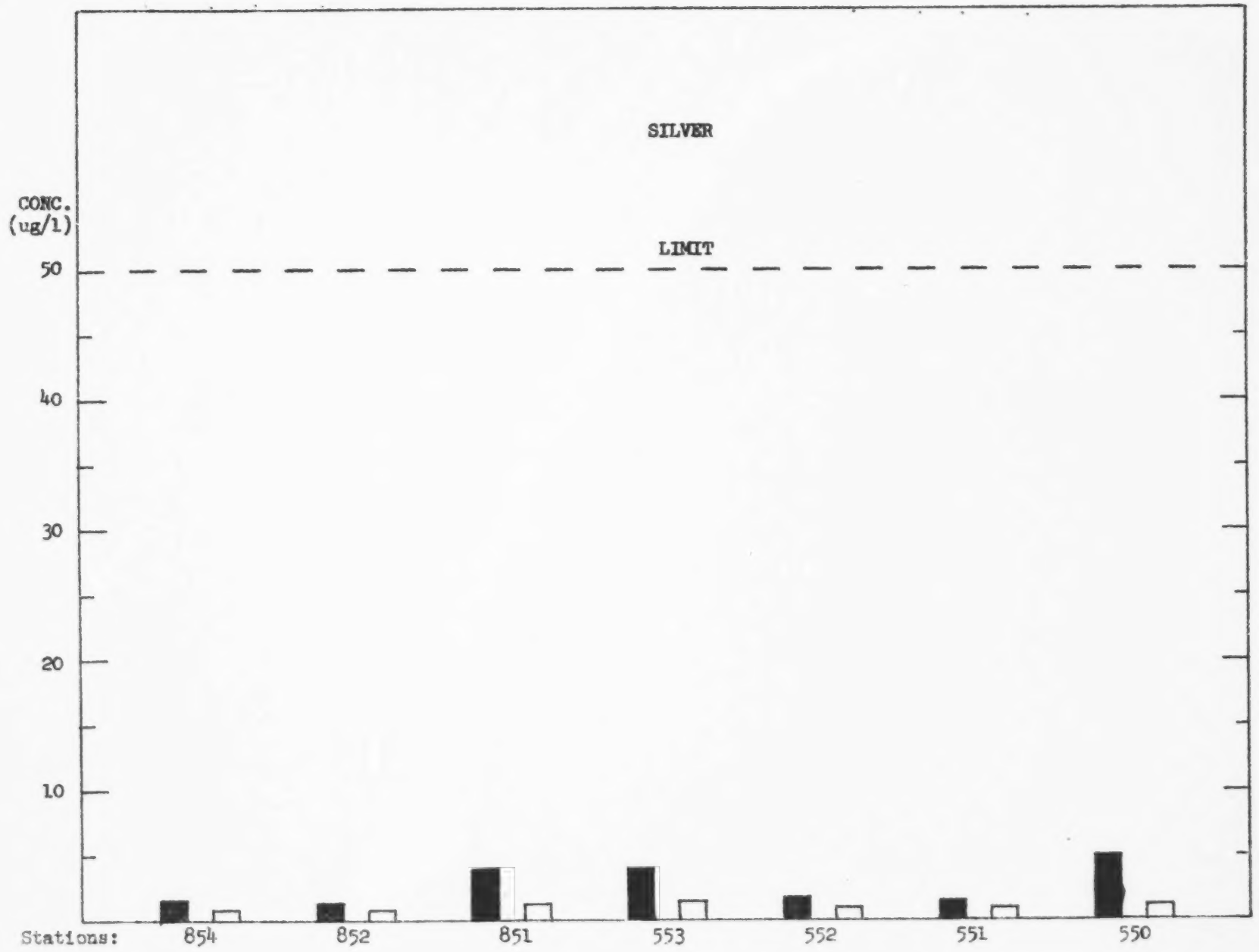
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CONC.
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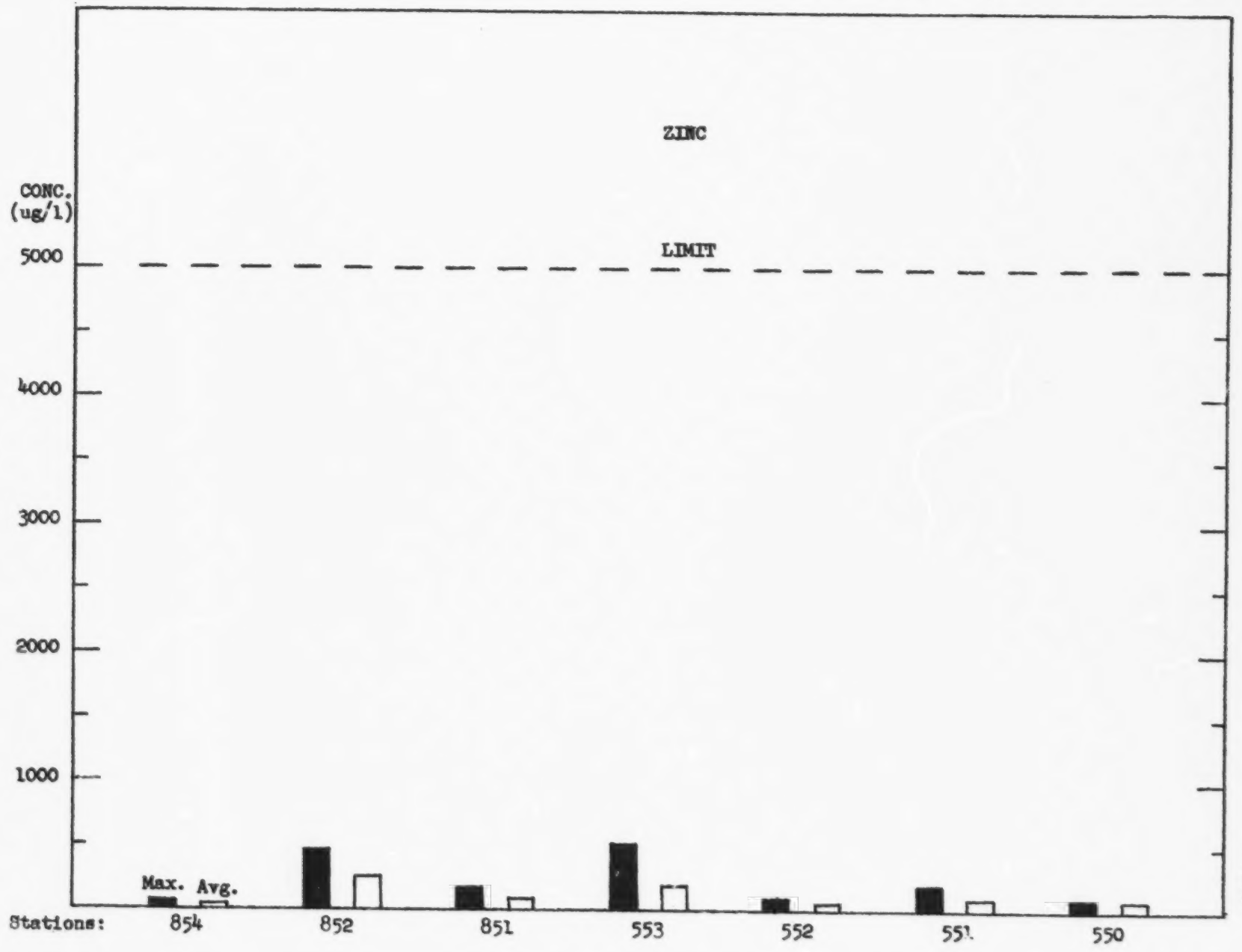
ZINC
CONC. (ug/l)
LIMIT
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4000
3000
2000
1000
Max.
Avg.
Stations:
854
852
851
553
552
551
550

APPENDIX C

Trace Metal Characteristics

ALUMINUM

One of the most abundant elements on the face of the earth, aluminum occurs in many rocks and ores but never as a pure metal in nature. Although the metal itself is insoluble, many of its salts are readily soluble. Other aluminum salts, however, are quite insoluble and consequently aluminum is not likely to occur for long in surface waters because it precipitates and settles or is absorbed as aluminum hydroxide, aluminum carbonate, etc. In streams the presence of aluminum ions may result from industrial wastes or more likely from wash water from water-treatment plants.

Domestic Water Supplies

As one of the most abundant elements, aluminum is a constituent of all soils, plants, and animal tissues. The total aluminum in the normal diet has been estimated at 10 to 100 mg per day. Very little of the ingested aluminum is absorbed in the alimentary canal and consequently it is almost entirely evacuated.

Aluminum in public supplies is not considered a public-health problem, at least when it is the result of treatment processes.

ARSENIC

Arsenic is found to a small extent in nature in the elemental form, usually associated with mine drainage. Arsenic is used in metallurgy to increase hardening and heat resistance, in glassware and ceramics, in tanneries, in dye manufacture, and in chemical industries. Its major use, however, has been for pesticides and as a wood preservative. Elemental arsenic is insoluble in water, but many of the arsenates are highly soluble.

Domestic Water Supplies

Although arsenic compounds are constantly taken into the body as a constituent of food, there is no evidence that arsenic is an essential element in human nutrition. Normal human blood contains 200 to 1000 ug/l of arsenic. It is found naturally in many foods such as vegetables and fruit. It also occurs as a residue on sprayed fruits and vegetables for which the U. S. Food and Drug Administration has set a limit of 3,500 ug/kg. The Food Standards Committee for England and Wales put into effect on August, 1959, a new regulation for arsenic limiting ready-to-drink beverages to 100 ug/l.

Arsenic is notorious for its toxicity to humans. Ingestion of as little as 100,000 ug usually results in severe poisoning and as little as 130,000 ug has proved fatal. Arsenic accumulates in the body, so that small doses may become fatal in time. A single dose may require ten days for complete disappearance and this low excretion is the basis for the cumulative toxic effect. Chronic arsenosis is of slow onset, and may not become apparent for two to six years. Small eruptions occur on the hands and the soles of the feet. In water taken over a long period of time the following concentrations

of arsenic have been reported as poisonous to human beings: 210 to 10,000 ug/l. On the other hand, the following concentrations have been reported in the literature as being safe in drinking water: 50 to 250 ug/l. In some parts as high as 1000 ug/l of arsenic has been suitable for several months on a temporary basis.

In 1942 for the first time, the USPHS Drinking Water Standards prescribed a maximum permissible concentration of 50 ug/l, which is still in effect. However, in 1962 a recommended limit of 10 ug/l was added to the mandatory limit. The World Health Organization International and European Drinking Water Standards prescribe a maximum allowable concentration of 200 ug/l.

BARIUM

This yellowish-white alkaline-earth metal is rapidly decomposed by water to form barium ions. It is found in nature as barytes, $BaSO_4$, witherite, $BaCO_3$, and other ores. Many of its salts are soluble, but the carbonate and sulfate are highly insoluble; consequently, it is to be expected that any barium ions discharged to natural waters will be quickly precipitated and removed by adsorption or sedimentation. Barium ions are not normally present in natural ground and surface waters in measurable concentration although they have been detected in a few springs and in effluents from areas where the ores are mined.

Barium and its salts are used in the metallurgical industry for special alloys, in the paint industry as a constituent of cements designed to withstand salt water, and in the ceramic and glass industries.

Domestic Water Supplies

Neither WHO International or the WHO European Drinking Water Standards prescribes a recommended or maximum limit for barium; and until 1962 there was no limit in the USPHS Drinking Water Standards. At that time a rejection limit for a water supply of 1000 ug/l was established, presumably because of possible toxic effects on the heart, blood vessels, and nerves.

BERYLLIUM

Beryllium, a relatively rare element, is not likely to occur in natural waters. Although the chloride and nitrate are very soluble in water and the sulfate moderately so, the carbonate and hydroxide are almost insoluble in cold water. Beryllium is used primarily in metallurgy to produce special alloys, in the manufacture of X-ray diffraction tubes and electrodes for neon signs, and in nuclear reactors.

Domestic Water Supplies

Until 1953 there was no reported indication that beryllium in any form is harmful when taken internally through the digestive tract. On the other hand, beryllium has been incriminated in pulmonary ailments of workers exposed to beryllium dust.

Following the development in 1947 of spectrochemical techniques for detecting beryllium in air, there has been a substantial increase in the number of beryllium poisoning cases reported in the literature.

Absorption of beryllium from the alimentary tract is slight (about 0.006 percent of that ingested) and excretion is fairly rapid.

BORON

Never found in nature in its elemental form, boron occurs as sodium borate (borox) or as calcium borate (colemanite) in mineral deposits and natural waters of southern California and in Italy. Elemental boron is used in nuclear installations as a shielding material (neutron absorber). It is also used in metallurgy to harden other metals.

Boric acid and boron salts are used extensively in industry for weather-proofing wood, fireproofing fabrics, manufacturing glass and porcelain, production of leather and carpets, cosmetics, photography, artificial gems, and many other purposes. Boric acid is used as a bactericide and fungicide. Finally, boron in the form of boron hydrides or borates is used in high-energy fuels.

Domestic Water Supplies

Although boron is essential in the nutrition of higher plants, there is no evidence that it performs any vital function in human or animal nutrition. It is present in the ordinary human diet to the extent of 10,000 to 20,000 ug/day, with fruits and vegetables as the highest contributors. In food or in water it is rapidly and completely absorbed by the human system, but it is also promptly excreted.

The ingestion of excessive doses of borates may cause nausea, cramps, convulsions, coma, and other symptoms of distress. The fatal dose for adults has been reported as 5 to 20 grams and as 20 to 45 grams. Above 30,000 gu/l boron may interfere with digestion as it acts as a food preservative.

CADMIUM

In the elemental form, cadmium is insoluble in water. It occurs in nature largely as the sulfide salt, greenockite or cadmium blend, often as an impurity in zinc-lead ores. Cadmium is used in metallurgy to alloy with copper, lead, silver, aluminum, and nickel. It is also used in electroplating, ceramics, pigmentation, photography, and nuclear reactors. Cadmium salts are sometimes employed as insecticides and antihelminthics.

Although the chloride, nitrate, and sulfate of cadmium are highly soluble in water, the carbonate and hydroxide are insoluble; hence, at high pH values, cadmium will be precipitated. Cadmium salts may be found in wastes from electroplating plants, pigment works, textile printing, and chemical industries.

Domestic Water Supplies

Cadmium poisoning of humans has resulted from the consumption of foods or liquids prepared and left in cadmium-plated containers. Cadmium-contaminated ice cubes in cold drinks have caused acute gastritis symptons within one hour.

Cadmium tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans. Once it enters the body, it is likely to remain. Normally, many plant and animal tissues contain about 1000 ug of cadmium per kg of tissue, but there is no evidence that cadmium is biologically essential or beneficial. The daily intake of cadmium in man can vary from 4 to 60 ug, depending on the foods chosen. The major sources appear to be seafoods and grains.

Human beings have been sickened by 13,000 to 15,000 ug/kg of cadmium in popsicles, 67,000 ug/l in punch, 300,000 ug/l in a cold drink, and 530,000 ug/kg in gelatin. As little as 14,500 ug of cadmium taken orally has caused nausea

and vomiting. According to the literature four members of a family whose drinking water contained 47 ug/l of cadmium had no history of adverse effects.

Prior to 1950, the USSR established the maximum permissible concentration of cadmium in domestic supplies at 100 ug/l. The 1962 Drinking Water Standards of the USPHS set a mandatory limit of 10 ug/l for cadmium and the World Health Organization European Standards prescribed a tolerance limit of 50 ug/l.

CHROMIUM

Chromium ions in both the trivalent and hexavalent forms are found in water. Of the trivalent chromic salts, the chloride, nitrate and sulfate are readily soluble in water, but the hydroxide and carbonate are quite insuluble. Of the hexavalent chromate salts, only sodium, potassium, and ammonium chromates are soluble. The corresponding dichromates are also quite soluble.

Hexavalent chromium salts are used extensively in metal pickling and plating operations, in anodizing aluminum, in the leather industry as a tanning agent, in the manufacture of paints, dyes, explosives, ceramics, and paper. Trivalent chromium salts, on the other hand, are used much less extensively, being employed as mordants in textile dyeing, in the ceramic and glass industry, and in photography.

Domestic Water Supplies

The USPHS Drinking Water Standards of 1962 set a rejection limit for a water supply of 50 ug/l for hexavalent chromium but none for trivalent. The WHO International and WHO European Drinking Water Standards also prescribe a limit of 50 ug/l for hexavalent chromium.

COBALT

Cobalt and its salts are used for making alloys, in nuclear technology, as pigment in the china and glass industry, and as binders in the tungsten-carbide tool industry.

Cobalt salts are divalent or trivalent. Solutions containing cobaltous ions are relatively stable but cobaltic ions are powerful oxidizing agents and consequently, they are unstable in natural waters.

Domestic Water Supplies

It has been reported that cobalt has a relatively low toxicity to man, and that traces of cobalt are essential to nutrition. The ingestion of soluble salts in sufficient concentrations, however, produces nausea and vomiting by local irritation. A maximum safe concentration of cobalt in drinking water can not be established or estimated on the basis of present knowledge. No literature relative to taste or color thresholds was uncovered.

COPPER

Copper salts occur in natural surface waters only in trace amounts, up to about 0.05 mg/l, so that their presence is generally the result of pollution, attributable to the corrosive action of the water on copper and brass tubing, to industrial effluents, or frequently to the use of copper compounds for the control of undesirable plankton organisms.

Because copper in concentrations high enough to be dangerous to human beings renders water disagreeable to taste, it is believed that copper is probably not a hazard in domestic supplies. However, copper in water may be disadvantageous or detrimental for certain industrial uses; and although in trace amounts copper may be beneficial or even essential for the growth of living organisms, in excessive quantities it has been found toxic to a wide variety of aquatic forms.

Domestic Water Supplies

Copper is found in traces in all plant and animal life, and it is believed to be essential for nutrition. The physiological function of copper appears to be involved in the metabolism of iron, for the utilization of iron by the blood-forming organs does not occur properly in the absence of copper.

Copper is not considered to be a cumulative poison such as lead or mercury. The limiting factor in domestic water supplies is taste with a limit of 1000 ug/l.

IRON

Metallic iron and its common alloys are of interest in this survey primarily because they are corroded by water in the presence of oxygen. The resulting products of corrosion, in which the iron is in the ionic or molecular state, may themselves be pollutants of water. In addition to corrosion products, natural water may be polluted by iron-bearing industrial wastes such as those from pickling operations and by the leaching of soluble iron salts from soil and rocks, e.g. acid-mine drainage and iron-bearing ground water. Many ferric and ferrous salts such as chlorides are highly soluble, but the ferrous ions are readily oxidized to ferric and form insoluble hydroxides.

Domestic Water Supplies

The 1962 Drinking Water Standards of the USPHS included a recommended limit of 300 ug/l for iron. The 1958 WHO International Standards contain a "permissible limit" of 300 ug/l and an "excessive limit" of 1000 ug/l.

These standards were not based upon physiological considerations, for iron in trace amounts is essential for nutrition. The daily nutritional requirement is 1 to 2 mg, and most diets contain 7 to 35 mg/day, with an average 16 mg/l. Consequently, drinking water containing iron in unpalatable and unesthetic concentrations, say 1000 ug/l, would have little effect on the total daily intake.

LEAD

Some natural waters contain lead in solution, as much as 400 to 800 ug/l, where mountain limestone and galena are found. In the U. S. A., lead concentrations in surface and ground waters used for domestic supplies range from traces to 0.04 mg/l averaging about 0.01 mg/l. Lead may also be introduced into water as a constituent of various industrial and mining effluents, or as a result of the action of the water on lead in pipes.

Domestic Water Supplies

Foreign to the human body, lead is a cumulative poison which tends to be deposited in bone. Typical symptoms of advanced lead poisoning are constipation, loss of appetite, anemia, abdominal pain, and tenderness, pain, and gradual paralysis, in the muscles, especially of the arms. Lead poisoning usually results from the cumulative toxic effects of lead after continuous consumption over a long period of time, rather than from occasional small doses.

The mean daily intake of lead by adults in North America is about 330 ug. Of this quantity, 10 to 30 ug per day are derived from water used for cooking and drinking. For many years, the USPHS rejection limit for a water supply for lead was 100 ug/l, but in the 1962 Standards, the limit for lead was reduced to 50 ug/l.

MANGANESE

Manganese is not found pure in nature, but its ores are very common and widely distributed. The metal or its salts are used extensively in steel alloys, for dry-cell batteries, in glass and ceramics, in the manufacture of paints and varnishes, in inks and dyes, in matches and fireworks, and in agriculture to enrich manganese-deficient soils. Like iron, it occurs in the divalent and trivalent forms. The chlorides, nitrates, and sulfates are highly soluble in water; but the oxides, carbonates and hydroxides are only sparingly soluble. Therefore, manganese is rarely found in surface waters in concentrations above 1.0 mg/l. In ground waters subject to reducing conditions, manganese can be leached from the soil and occur in high concentrations.

Domestic Water Supplies

The 1962 Drinking Water Standards of the USPHS set a recommended limit for manganese of 50 ug/l. The 1958 WHO International Standards prescribe a "permissible limit" of 100 ug/l and an "excessive limit" of 500 ug/l.

These standards have been established on the basis of esthetic and economic considerations rather than physiological hazards. Diets deficient in manganese result in impaired or abnormal growth, symptoms of central nervous system disorders, anemia, and possibly interference with reproductive functions. The daily intake from a normal diet is about 10 mg. It is absorbed very slightly, and deposits mainly in the liver and kidneys.

MOLYBDENUM

This metal and its salts are not considered to be significant in water pollution at the present time. Although the element occurs in such minerals as molybdenite, MoS_2, and unilfenite, $PbMoO_4$, it is not widely distributed in nature. The metal and its salts are used principally for metallurgy and for electrical and electronic apparatus.

It is also used in the glass and ceramic industries, for the production of pigments, and as a constituent of fertilizers for leguminous crops.

NICKEL

Elemental nickel seldom occurs in nature, but nickel compounds are found in many ores and minerals. As a pure metal it is not a problem in water pollution because it is not affected by, or soluble in, water. Many nickel salts, however, are highly soluble in water and since they are used in metal-plating works they may be discharged to surface or ground waters.

Domestic Water Supplies

The USPHS Drinking Water Standards do not place any limit on nickel but Kirkor reports that in Russia the maximum permissible concentration is 1000 ug/l. According to Sawyers and Brown the existence of 90 ug/l of copper 80 ug/l of cobalt and 30 ug/l of nickel in public water supplies containing 80 to 90 mg/l of total solids, 4.4 mg/l of chlorides and with a pH of 3.8 to 4.5 caused pitting of aluminum in the kettles. Without these traces no pitting occurred.

No data on the toxicity of nickel to man were revealed, but the toxicity is believed to be very low. Systemic poisoning of human beings by nickel or nickel salts is almost unknown.

SILVER

Silver can be leached from its ores by ground water or surface water, but since many of these salts are insoluble, silver ions cannot be expected to occur in significant concentrations in natural waters.

Silver metal is used in jewelry and silverware, in alloys, for electroplating, and in the processing of food and beverages. Silver nitrate is used in photography, ink manufacture, electroplating, coloring porcelain, and as an antiseptic. From such sources, traces of silver can be expected to reach natural waters.

Domestic Water Supplies

Prior to 1962 no restriction was placed on silver in the USPHS Drinking Water Standards, nor does any limitation presently appear in the WHO International or European standards. The 1962 edition of the USPHS Standards sets a rejection limit for a water supply of 50 ug/l of silver. Presumably this was not set because of the danger of naturally occurring silver, but to prevent its intentional addition to water, in excessive amounts, for disinfection.

The chronic administration of silver salts, not uncommon in the early part of the 20th Century, led to a bluish permanent darkening of the skin. With prolonged administration of silver salts, a small proportion is absorbed and deposited in the skin where it is reduced by light to metallic silver.

STRONTIUM

Related to calcium, magnesium and barium, this element is not found free in nature. It occurs largely with calcium or barium minerals in the form of the sulfate or the carbonate. The carbonate is soluble only to the extent of about 10 mg/l and the sulfate to about 114 mg/l. Hence, strontium is not likely to occur in high concentrations in surface waters. It is not adsorbed readily by soils and hence strontium may be expected to travel readily along with ground waters.

Stontium metal is used in some alloys of tin and lead. The salts are used in pyrotechnics, in refining beet sugar, in manufacturing glass and paints, in ceramics and in some medicines.

Strontium is present in plant and animal tissues in trace concentrations, but it occurs in much higher concentrations in bone structures. There is no evidence that strontium is essential for plant nutrition, but there are indications that it is necessary for the growth of animals and especially for calcification of bones and teeth.

Toxicologically, no evidence was uncovered to show that non-radioactive strontium salts taken orally by man or animals produces deleterious action. In deed, strontium bromide has been used medicinally as a sedative and anti-epileptic; strontium iodide has been used in iodine therapy, and strontium lactate for osteoporosis.

VANADIUM

Metallic vanadium does not occur free in nature but minerals containing vanadium are widespread. The metal is used in metallurgy to increase the hardness and malleability of steel, and the salts are used in the manufacture of glass, in photography, and as a mordant in dyeing and printing fabrics.

In its salts, vanadium may have valances of 2, 3, 4 and 5. The tetra- and penta-salts are generally soluble, but the trifluoride, trioxide, and trisulfide are insoluble. Vanadium forms the vanadyl cation (VO) the salts of which are soluble. It also forms the anion vanadate (VO_4). It is likely, therefore, that any vanadium salts, occurring in waste water will remain in solution.

It has been reported that vanadium in drinking water at concentrations of 30 to 22 ug/l reduced the incedence of dental caries in both primary and permanent teeth.

ZINC

Occurring abundantly in rocks and ores, zinc is readily refined into a stable pure metal and it is used extensively for galvanizing, in alloys, for electrical purposes, in printing plates, for dye-manufacture and for dyeing processes, and for many other industrial purposes. Zinc salts are used in paint pigments, cosmetics, pharmaceutics, dyes, insecticides, and other products too numerous to list herein. Many of these salts are highly soluble in water; hence, it is to be expected that zinc might occur in many industrial wastes. On the other hand, some zinc salts are insoluble in water and consequently, it is to be expected that some zinc will precipitate and be removed readily in most natural waters.

Domestic Water Supplies

The U. S. Public Health Service Drinking Water Standards of 1962 set a limit of 5000 ug/l of zinc in acceptable water supplies when no alternate sources are available.

Zinc has shown no adverse physiological effects upon man except at very high concentrations. In fact, zinc is an essential and beneficial element in human nutirtion. The normal human intake of zinc is estimated at 10-15 mg per day. A summary of literature relating to the toxicity of zinc reveals that families and communities have used waters containing up to 26,600 ug/l with no ill effects. On the other hand, another supply containing 30,800 ug/l caused nausea and fainting spells.